

Studies on The Distribution Of Particulate Trace Metal Like Chromium in Visakhapatnam Harbor Waters, India

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Abstract - Industrialization and urbanization of Visakhapatnam plays a major role in polluting Visakhapatnam harbor waters. It is due to more amount of domestic sewage, industrial, agricultural effluents are polluting the harbor waters. It is very important to study the distribution of metals like cadmium and copper in highly polluted Visakhapatnam harbor waters is essential to assess their presence in the bio-geocycles, their possible accumulations in organisms, and transfer to human beings through food chains, so far there are single detailed seasonal and spatial studies of trace metals like cadmium and copper in the distribution of Visakhapatnam harbor waters, the author has therefore been taken up the present investigation on total suspended particulate matter at all five stations.

Key words: Harbor waters, Geo cycle, Particulate matter, Heavy metals.

I. INTRODUCTION

India is a country developing fast industrially and agriculturally. A consequence of the former is urbanization and of the latter, denudation of the forest cover. Both have a telling effect on the quality of the environment. The sea, which represents a regime of the lowest potential energy, receives all types of influxes carrying industrial, agricultural and urban wastes; hence its water quality is affected and thereby its living organisms. Unlike in the case of seas, e.g., the Mediterranean bordering highly industrialized countries, Indian seas are not as much polluted by these effluents, except at certain point locations (a recent review on present status of marine pollution (Qasim & Sen Gupta, 1980;). This is a good starting point for evolving (and implementing) methods of pollution abatement followed by a long-term protection policy of the coastal waters. Usually, many industries are located on river banks, back waters and harbors etc., for an easy disposal of their wastes. The harbors in addition to being used as ports are often used as points of discharge of effluents from industries, sewage and agriculture, etc. In recent years there has been a rapidly growing interest on the study of heavy metal content in coastal and harbor, its behavior and the pathways by which they are introduced into the system. Well known that harbors and estuaries of the world are the region heaviest pollution by heavy metals (Forstner and Wittmann, 1981). The physicochemical processes which act soil of the catchment area normally control the concentration of trace metals in the fluvial and sediments. Due to anthropogenic input, abnormal concentration of heavy metals in both dissolved and particulate phases of the harbor waters. These high inputs can also affect the adjoining coastal waters due to exchange. Addition of these undesirable heavy metals in

excess quantities can disrupt the delicate balance which exist between biomass and trace metals. When it exceeds tolerance level, certain species in aquatic organisms will perish. Certain aquatic organisms have the ability to concentrate toxic metals many fold in their body which ultimately passes on to human beings through marine food web causing deleterious effects to human beings.

II. MATERIALS AND METHODS

Visakhapatnam harbor is divided into 5 stations they are,

Station 1, is located in the centre of the **outer harbor**. The average depth of this station is about 18 meters. A finger type Jetty is situated in this region for loading iron ore into export vessels of as high as 1 lakh DWT.

Station 2, is located in the centre of the **entrance channel**. This is a confluence point between outer harbor and inner harbor. The average depth of this channel is 10.7 m.

Station 3, is located in the centre of the **western arm** (WA, 0.88 km in length, 91 m in width and 10.7 m in depth) of the inner harbor. This is one of the three navigable arms of Visakhapatnam harbor.

Station 4, is located in the centre of the **northwestern arm** (NWA) of the inner harbor, which is the principal source of industrial effluents. A monsoon fed stream. 'Meghadrigedda' opens into this arm on the western side. The average depth of this arm is 10 meters.

Station 5, is located at the end of the **northern arm** (NA) which is the main commercial navigational channel of the inner harbor. The channel is about 152.4 m in width with an average of 10.7 m in depth.

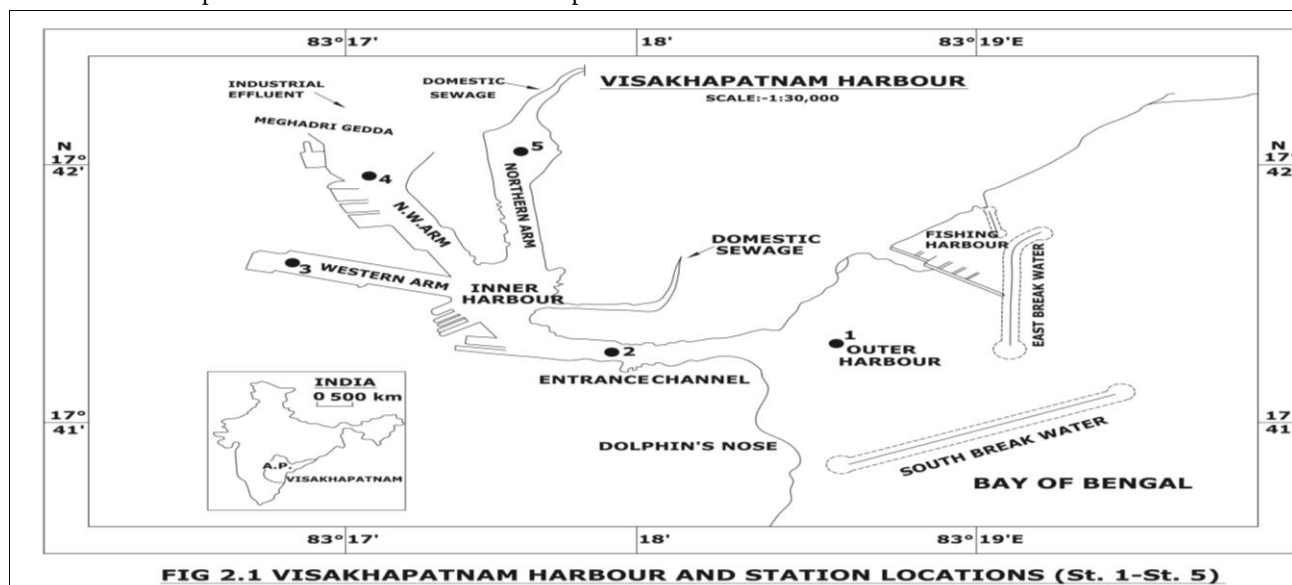
A hired mechanized boat with no laboratory facilities was used for collection of samples. All photometric

measurements were carried out on a Shimadzu Spectrophotometer (UV 260) using 1 or 5 cm path length cells. Particulate metals were analyzed on Orion Atomic Absorption Spectrophotometer after proper digestion.

Solvents like acetone, chemicals and acids used in the investigations were all of E-Merck analytical reagent grade. Double distilled water or de-ionized water was used in the estimation of trace metals and inorganic constituents except for ammonium ion for which ammonia free water was prepared by redistilling distilled water after treatment with potassium persulphate (1.5 g/L) and concentrated sulphuric acid (1 ml/L) was used.

Particulate matter was collected separately on a total of 2 filters at each station and season, one is on 0.45 μm Membrane Millipore HA filter for total suspended

particulate metals and other is on GF/F (0.7 μm) for chlorophylls. Millipore filtration apparatus was used for this purpose with a gentle vacuum. The volume of water that was filtered varied from 0.5 to 1.0 liters depending on the turbidity of the sample and its particulate content. All filters were washed with Milli Q water to remove salts and were kept frozen until further analysis. Surface and bottom water samples were collected. Surface waters were collected with a clean plastic bucket and bottom waters were collected Niskin bottom water sampler, they were immediately filtered through Glass fiber GF/F filters papers. The filtered waters are used for the determination of spatial and seasonal distribution of particulate trace metals like Chromium.



III. RESULTS AND DISCUSSION

Harbor, coastal waters and estuaries act as transition zone in which continental material is trapped and through which some of the material is transported to the open Sea. The chemical composition and variability of suspended particulate matter (SPM) in harbor and coastal water is controlled by complex interplay of physical and biogeochemical processes. Some of the most important geochemical processes influencing variability are mixing of land and riverine suspended matter with marine material, flocculation of colloidal materials (Benoit *et al.*, 1994), adsorption and desorption in low salinity zone (Windom *et al.*, 1988; Zwolsman *et al.*, 1997), production of organic matter by phytoplankton (Balls, 1990; Burton *et al.*, 1994), mobilization of Fe-Mn oxides in reducing sediments (Feely *et al.*, 1986) and re-suspension of bottom sediments (Balls, 1994; Hatjeet *et al.*, 2001). It is not surprising, that studies of metal behavior in polluted harbor and coastal waters have well documented, but there is a substantial difference from one area to another area. Studies of particulate trace metals are usually based on a single, or a small number of surveys. Moreover, the concentration of particulate metals can be

variable, both as a result of changing inputs and or seasonal effects involving biological, geochemical and physical interactions.

Numerous studies on the distribution and behavior of trace metals in various coastal and harbor waters in different parts of the world have revealed that individual metals exhibit contrasting behavior between areas. Factors which have been demonstrated to be important in controlling trace metal behavior include flushing time (Morris, 1990; Owens and Balls, 1997). Very few studies have been made on the distribution of trace metals in the Visakhapatnam harbor and coastal waters. Satyanarayana *et al.*, (1985) studied on the distribution of particulate and dissolved metals in Visakhapatnam harbor waters. Sen Gupta *et al.*, (1978) studied the trace metal analysis in the Arabian Sea water. Sanzgiri and Mores (1979) Studied the trace metal distribution in the Laccadive Sea. Braganca and Sanzgiri (1980) studied the concentrations of few trace metals in coastal and offshore regions of the Bay of Bengal. Rajandran *et al.*, (1982) studied the dissolved and particulate trace metals in western Bay of Bengal. Jegatheesan and Venugopalan (1973) studied the trace elements in the particulate matter of Porto Novo waters.

Information on the distribution of metals in polluted harbor like Visakhapatnam harbor is essential to assess their involvement in the biogeochemical cycles, their possible accumulations in organisms, and their transfer to human beings through food chain. So far there are single detailed seasonal and spatial studies of trace metal distribution in the Visakhapatnam harbor waters, the author has therefore been taken up the present investigation to assess the spatial and seasonal distribution of particulate trace metals like

Chromium in the harbor waters along with hydrological and nutrient constituents covering the five stations.

1. TOTAL SUSPENDED PARTICULATE MATTER

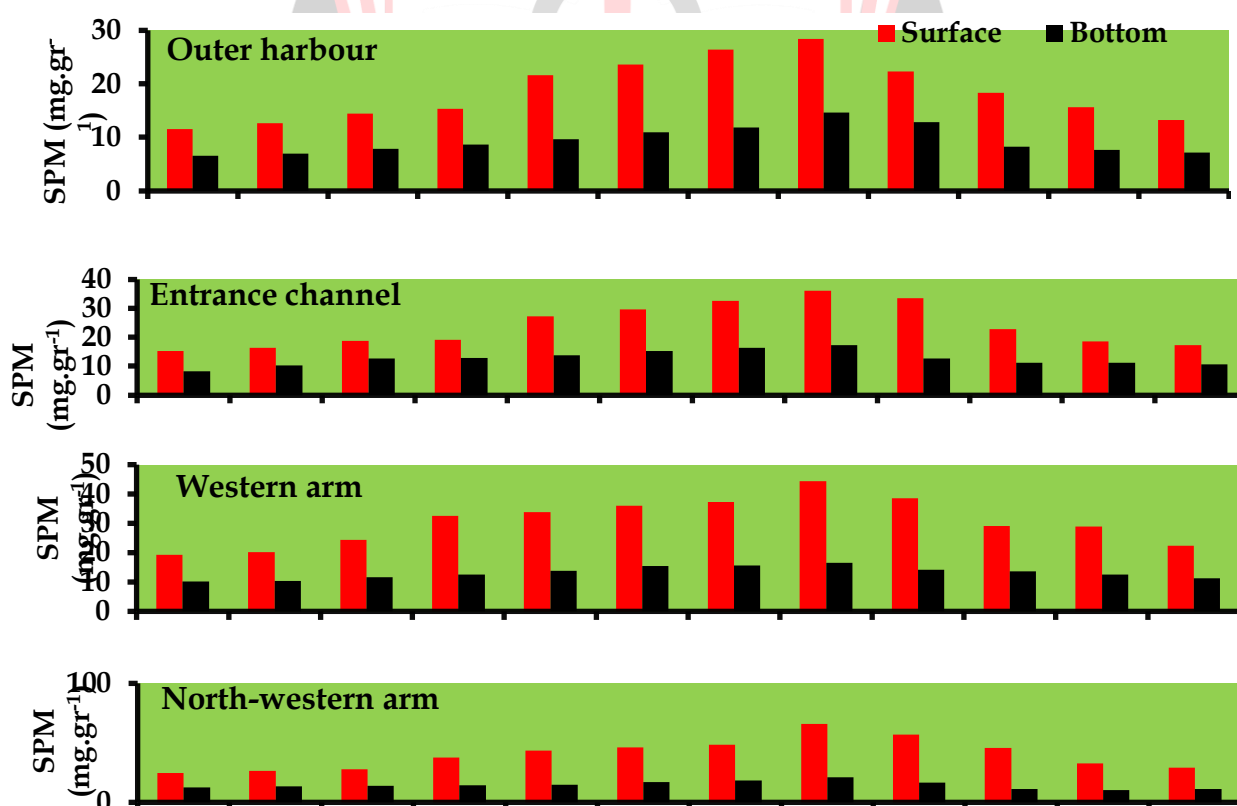
The station-wise summary statistics on total suspended particulate matter (TSPM) in the Visakhapatnam harbor waters during the study period are given in Table.1 The detailed seasonal distribution at five individual all stations are shown in Fig.1.

TABLE 1 STATION – WISE SUMMARY STATISTICS OF SPM (MG.GR⁻¹) IN THE VISAKHAPATNAM HARBOR WATERS

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Outer harbor	11.15	28.41	18.63	5.70	6.58	14.65	9.42	2.60
Entrance channel	15.25	36.13	23.94	7.47	8.22	17.25	12.68	2.63
Western arm	19.21	44.29	30.54	7.89	10.23	16.53	13.19	2.07
Northwestern arm	24.57	65.85	40.28	12.96	10.25	21.15	14.52	3.25
Northern arm	21.16	42.41	28.86	6.63	10.91	24.28	16.62	4.67

The TSPM values in the surface waters varied from 11.55 to 65.85mg.gr⁻¹ with an average of 28.45mg.gr⁻¹ where as in the bottom waters, the TSPM varied from 6.58 to 24.28mg.gr⁻¹ with an average of 13.29mg.gr⁻¹. In general, total suspended particulate matter showed relatively higher values in surface when compared with those in bottom waters. This may be due to the land runoff associated with

biological and anthropogenic activity. Seasonally higher TSPM values (65.85 mg.gr⁻¹) were observed in the northwestern arm (St.4) during monsoon, which may be due to higher land runoff along with turbulent flow containing higher amount fluvial suspended matter at this station and decreased seaward by order of magnitude.



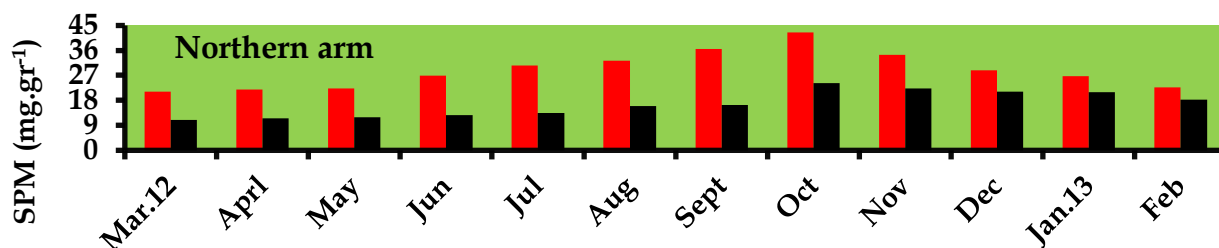


Fig. 1 Monthly Distribution Of Particulate Suspended Matter In The Visakhapatnam Harbor Waters (St. 1 - St. 5)

The present study reflects the decrease in suspended particulate matter with increase in salinity and this trend simply denotes the increase in the marine component. It might be argued that the decrease in particulate matter contents is also caused by desorption process. It follows that the decrease in the particulate matter with increasing salinity is primarily caused by mixing of fluvial matter with marine particulates.

1.1 Relation Of Suspended Particulate Matter With Ph

Significant negative correlations were observed between suspended particulate matter with pH of the harbor waters ($r = -0.87$, $p < 0.001$) is shown in Fig.2 From the above figure, it was observed that the concentration of TSPM decreases with increasing in pH of the harbor waters due to its flocculation at the outer harbor.

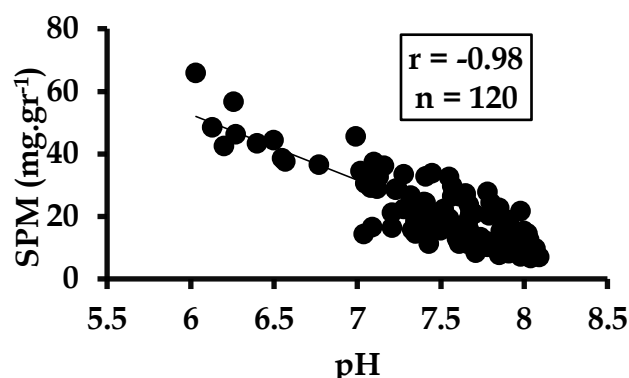


Fig. 2. Relation Between Tspm With Ph In The Visakhapatnam Harbor Waters

An increase in pH was observed during summer and this may be due to associated with photosynthesis of planktonic blooms. The lower pH values were observed during monsoon season due to the higher fresh water along with industrial and domestic sewage.

1.2. Relation Of Suspended Particulate Matter With Salinity

Significant negative relationship was observed between suspended particulate matter with salinity ($r = -0.72$, $p < 0.001$) in the present study is shown in Fig. 3. The decrease of suspended particulate matter with increasing salinity is primarily caused by mixing of fluvial matter with marine waters, and also caused by desorption of suspended particulate matter at higher salinities in the outer harbor area.

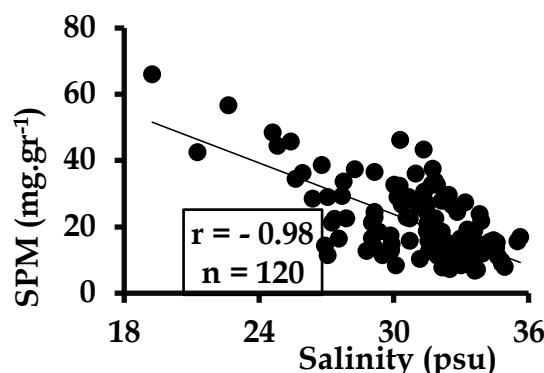


Fig. 3. Relation Between Tspm With Salinity In The Visakhapatnam Harbor Waters

3. PARTICULATE CHROMIUM

Chromium concentration in natural waters is usually very small. Elevated concentrations can result from industrial and mining process (Datar and Vashishtha, 1990). Chromium in water supplies is generally found in the hexavalent form (Thomas,1963).

The station-wise summary statistics on particulate chromium in the Visakhapatnam harbor waters during the study period was given in Table 4.3. The detailed monthly distribution chromium at five individual stations in both surface and bottom waters are shown in Fig. 7.

Table: 3. Station – Wise Summary Statistics Of Particulate Chromium ($\mu\text{g}.\text{Gr}^{-1}$) In The Visakhapatnam Harbor Waters.

Station	Surface				Bottom			
	Min.	Max.	Mean	S.D.±	Min.	Max.	Mean	S.D.±
Outer harbor	24.12	37.45	31.15	4.96	20.12	28.64	24.07	2.67
Entrance channel	26.81	40.98	33.75	4.24	21.21	31.25	26.01	3.03
Western arm	28.52	43.35	36.16	4.37	22.32	38.21	31.10	5.48
Northwestern arm	35.21	71.58	49.24	11.42	24.32	61.54	41.15	11.66
Northern arm	30.23	59.85	43.36	9.30	23.25	44.25	34.18	6.85

The particulate chromium concentrations in the surface waters of the Visakhapatnam harbor were in the range of 24.12 to 71.58 $\mu\text{g}.\text{gr}^{-1}$ with an average of 28.66 $\mu\text{g}.\text{gr}^{-1}$ where as in the bottom waters, its concentrations ranged

from 20.12 to 61.54 $\mu\text{g}.\text{gr}^{-1}$ with an average of 31.30 $\mu\text{g}.\text{gr}^{-1}$. Higher concentrations of particulate chromium were observed in the surface waters than that of bottom waters in all stations.

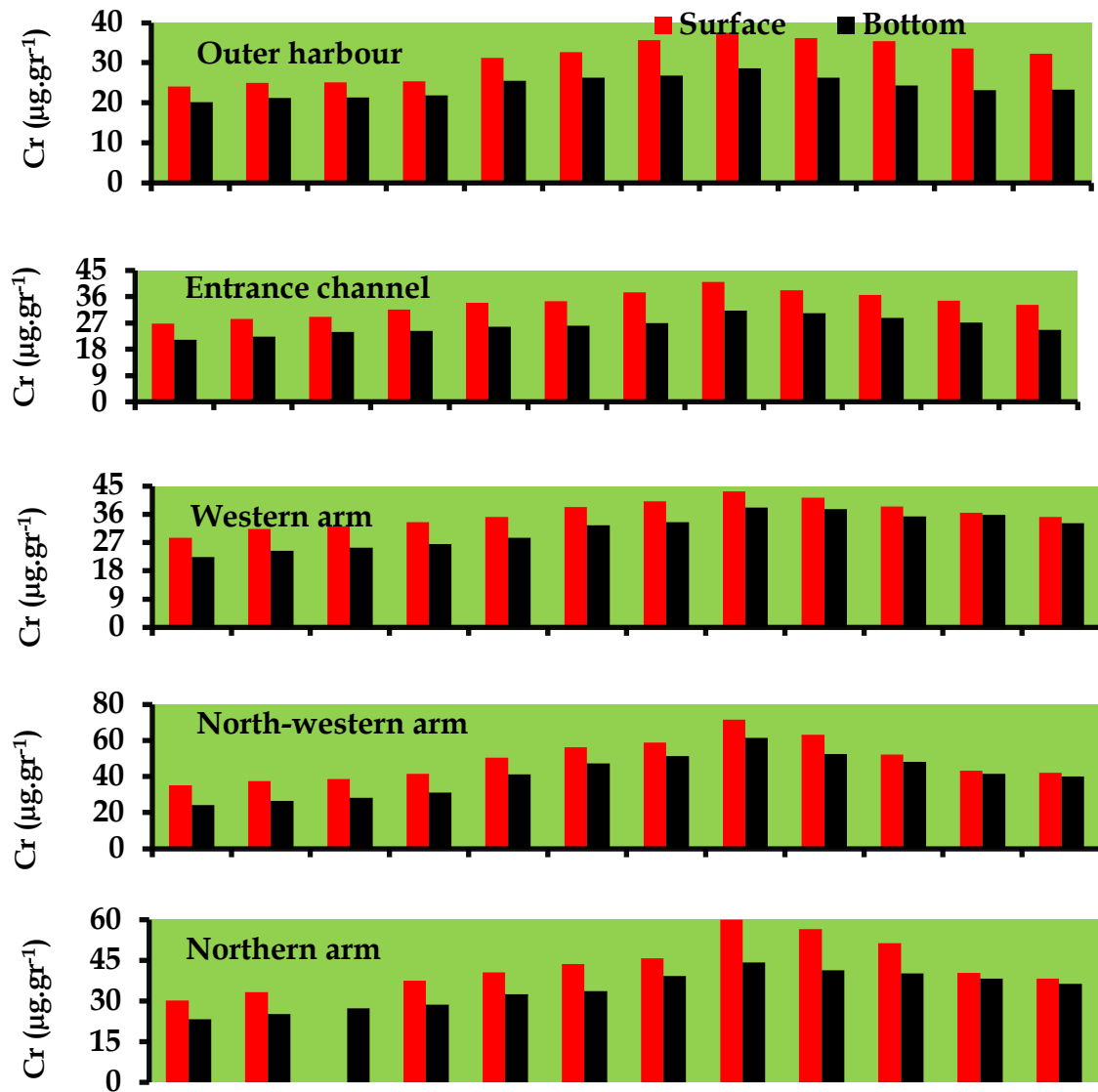


Fig. 7. Monthly Distribution Of Particulate Chromium In The Visakhapatnam Harbor Waters. (St.1 - St.5).

The concentrations of chromium observed in the present study are higher than river, estuarine and coastal waters reported elsewhere. Chromium distribution is well documented in the Amazon plume (Boyle *et al.*, 1982), in the Changjiang (Edmond *et al.*, 1985; Elbaz-Poulichet *et al.*, 1987), in the Gironde and Huanghe estuaries (Kraepiel *et al.*, 1997), in the Mississippi estuary (Shiller and Boyle, 1991) and in the lower part of the Scheldt estuary (Duinkeret *et al.*, 1982; Salomons and Kerdijk, 1986), in the surface waters off Pondicherry (Solaiet *et al.*, 2010), in the waters of Cochin estuary, and adjoining Periyar and Muvattupuzha rivers, in the surface waters of Ennore estuary (Rajkumaret *et al.*, 2011) and in the estuarine waters of Uppanar, Nagapattinam, India (Sankaret *et al.*, 2010). Seasonally, higher values were observed during monsoon season.

3.1. Relation Of Particulate Chromium With Ph

Significant inverse correlations were observed between the particulate chromium with pH in the Visakhapatnam harborwaters ($r = -0.99$, $p < 0.001$), is shown in Fig. 8

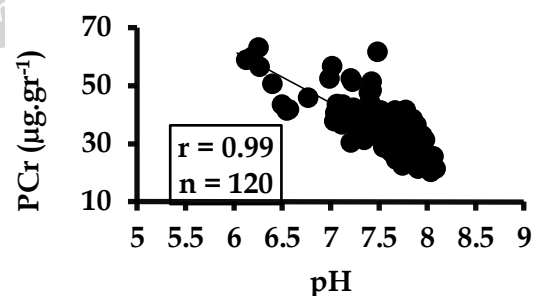


Fig. 8. Relation Between Ph And Particulate Chromium In The Visakhapatnam Harbor Water

It was observed that the particulate cadmium concentrations are decrease with increase in pH due to dilution of highly polluted inner harbor waters with less polluted outer harbor waters. Similar relationships between pH and particulate cadmium have been observed in the Scheldt estuary. Relatively higher pH values in the Visakhapatnam harbor waters were observed during pre-monsoon (summer) may be due to the influence of marine

water intrusion and also by photosynthetic activity by plankton blooms during this period.

The decrease of pH was also observed with increasing distance from the inner harbor. The influence of ionic strength on the dissociation constants of carbonic acid also contributes to the pH drop in the inner harbor waters and also discharge of acidic industrial effluents in to the inner harbor stations.

3.2. Relation Of Particulate Chromium With Salinity

Significant inverse correlations were observed between the particulate chromium with salinity in the Visakhapatnam harbor waters ($r = -0.99$, $p < 0.001$), is shown in Fig. 9

From the above figure it was observed that the concentrations of chromium decrease with increase in salinity. It is well known that with increase in salinity there is a greater desorption and solubilization of particulate metals

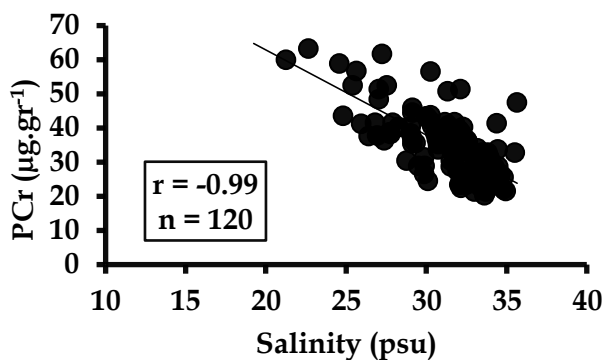


Fig. 9. Relation Between Particulate Chromium With Salinity In The Visakhapatnam Harbor Water

Similar relationships between salinity and particulate chromium have also been observed in the estuarine waters of Scheldt (Salomonset *al.*, 1981; Duinkeret *al.*, 1982. Regnier and Wollast, 1993) and in many estuaries in Europe and USA, (Olsen *et al.*, 1989; Schoer 1990; Turner *et al.*, 1991; Paalman and Vander Weijden, 1992), in the estuarine waters of Gironde (Krapielet *al.*, 1997), It is well known that these behaviors are primarily related to physical mixing of fluvial material with marine particulates at the mouth of the estuaries and also caused by flocculation and desorption of particulate metals into the bottom sediments (Zwolsmanet *al.*, 1999; Michel *et al.*, 2000; Tang *et al.*, 2002; Abdallah, 2008).

Seasonally higher concentrations particulate chromium were observed during monsoon and post-monsoon seasons, due to influx of high amounts industrial effluents and release of domestic sewage in to the harbor waters are more. Lower concentrations were observed during pre-monsoon season may be due to desorption and solubilization of particulate chromium as salinity increased in the waters of outer harbor is always connected to the coastal waters of Bay of Bengal.

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